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Synthesis and characterization of a thermally cross-linkable polyolefin from oleic acid

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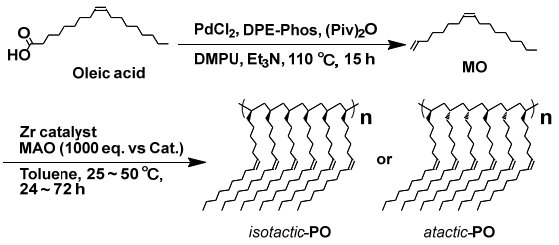
INTRODUCTION Bio-based compounds contain unique structures such as inner olefins, monocyclic and bicyclic structures, etc. These compounds have been recognized as key ingredients for specialty chemicals and have been widely used as food additives, plasticizer, cosmetics, fragrances, and essential oils.[1-3] Owing to their unique structures, these compounds are difficult to synthesize from petrochemicals. For instance, oleic acid synthesis from 1-decyne, which is a kind of petrochemical, is a six-step process.[4-5] Unprecedented functional polymers can be obtained from bio-based resources via utilization of their unique structures. Many researchers have investigated new polymer materials derived from bio-based resources like fatty acids, lactic acids, and hydroxyalkanoates. [6-10] Among various available bio-based resources, herein we focused on oleic acid ((9Z)-9-octadecenoic acid), a naturally occurring fatty acid, because it is abundantly available in olives and various industrial and agricultural food wastes.[11] There have recently been reports on the application of oleic acid as a feedstock for polymer materials;[8, 12] however, utilization of oleic acid must be developed further based on its unique internal olefin moiety in long alkyl chain, which is a structural feature not easily obtained from petroleum. Herein, we have introduced a chemical transformation of oleic acid to a novel polyolefin possessing an internal olefin moiety as a reactive functional group (Scheme 1). Since the conversion of oleic acid to (8Z)-1,8-heptadecadiene (**MO**) via catalytic decarbonylative elimination has been reported,[13-15] we envisioned the site-specific polymerization of **MO** to obtain a new functional polyolefin (**PO**). The internal olefin moiety in **PO** can be converted to various functional groups. Nomura reported that copolymerization of 1,7-octadiene with 1-octene afforded high-molecular-weight copolymers containing side chains bearing terminal olefins; hydroxyl groups can be quantitatively introduced into the terminal olefin moieties.[16] Selective 1,2-polymerization of 1,3-diene also affords polyolefins bearing olefinic side chains.[17-19] Coates and Grubbs reported a post functionalization of 1,2-polybutadiene using ring closing metathesis at the olefin moieties.[20] While most of reported reactive polyolefins contain terminal olefinic moieties in the side chain,[21-23] this study focuses on internal olefin moieties as a reactive functional group, which is expected to lead a new post functionalization methodology. To summarize, herein we report the molecular design of a novel functional polyolefin derived from oleic acid: an applicable synthesis and characterization of **PO** is presented. The thermal cross-linking reactions and adhesive properties of **PO** were also evaluated to elucidate the usability of the polymer.



SCHEME 1 Synthesis of **PO** from oleic acid.

RESULTS AND DISCUSSION

The transformation of oleic acid to **MO** was performed according to previous reports.[13-15] Pd-catalyzed decarbonylative elimination afforded **MO** in good yield (70%). Since **MO** has both terminal and internal olefin moieties, to obtain a structurally defined polymer material, its polymerization should proceed stereoregularly and site-selectively at the terminal olefin moiety. Previously, the Kaminsky group reported that C_2 symmetric bridged zirconocene complexes with methylaluminoxane (MAO) catalysts gave stereoregular polyolefins.[24] More specifically, the Wahner group reported the highly isotactically selective polymerization of 1-decene using Et(Ind)$_2$ZrCl$_2$/MAO catalyst.[25,26] Therefore, Et(Ind)$_2$ZrCl$_2$/MAO can facilitate the isotactic polymerization of **MO**. To confirm the site-selectivity of the polymerization, control experiments were conducted using a mixture of 1-decene and (6Z)-6-dodecene, giving isotactic poly-(1-decene) in good yield (Supporting Information, Scheme S1). This result indicated that the C_2 symmetric nature of Et(Ind)$_2$ZrCl$_2$ was efficient in the site-selective polymerization of **MO**. Next, to determine the appropriate polymerization conditions, polymerization of **MO** using the Et(Ind)$_2$ZrCl$_2$/MAO catalyst was performed under various conditions (Table 1). All the resulting polymers were transparent and viscous oily compounds. Low-molecular-weight polymers were obtained at entry 1 to 3 (Table 1). At a **MO**/catalyst ratio of 17000 (Table 1, entry 4), the corresponding polymer, with the highest molecular weight of 16400, was obtained in 80% yield. The number-averaged molecular weight of the polymer did not increase with the addition of **MO** (entry 5). In contrast, other Zr complexes produced less to no desired products. The polymerization of **MO** using the non-bridged C_{2v} symmetric (Ind)$_2$ZrCl$_2$/MAO catalyst[27] gave the corresponding polymer in moderate yield (entry 6), while Ph$_2$C(Cp)(9-fluolenyl)ZrCl$_2$ showed no catalytic activity toward **MO** (entry 7). Radical polymerization of **MO** was also investigated using AIBN as the catalyst; however, the reaction did not occur. Additional control experiments were also performed and are summarized in the ESI (Supporting Information, Tables S2 and S3).

The chemical structures of the synthesized polymers were elucidated using nuclear magnetic resonance (NMR) spectroscopy. Figure 1(a) and 1(b) shows the ^{1}H NMR spectra of **MO** and the obtained **PO** (entry 4, Table 1). While the terminal olefin signals of **MO** appeared at δ 4.9 ppm and δ 5.8 ppm (Fig. 1(a)), no terminal olefin signals were observed in the spectrum of **PO** (Fig. 1(b)). However, the peak corresponding to the inner olefin moiety remained at 5.3 ppm (Fig. 1(b)). ^{1}H NMR spectrum of the **PO** obtained using the (Ind)$_2$ZrCl$_2$/MAO catalyst (Table 1, entry 6) exhibited a pattern similar to that of **PO** obtained using the Et(Ind)$_2$ZrCl$_2$/MAO catalyst (Table 1, entry 4) (Supporting Information, Fig. S3). In addition, all ^{13}C{^{1}H} NMR signals of **PO** obtained using the Et(Ind)$_2$ZrCl$_2$/MAO catalyst were assigned to the carbons of the product (Supporting Information, Fig. S7-S10). Figure 1(c) shows the ^{13}C{^{1}H} NMR spectra of **PO** (entries 4 and 6, Table 1) at the pentad regions of the branched carbon atom. The sharp signal at δ 34.9 ppm in the ^{13}C {^{1}H} NMR spectrum of **PO** obtained using the Et(Ind)$_2$ZrCl$_2$/MAO catalyst (*iso*-**PO** in Figure 1(c)) indicated high isotacticity of the polymer (*iso*-**PO**). In contrast, the ^{13}C {^{1}H} NMR spectrum of **PO** prepared using the (Ind)$_2$ZrCl$_2$/MAO catalyst (entry 6, Table 1) displayed broad and complicated signals in the same region (*ata*-**PO** in Fig. 1(c), Supporting Information, Fig. S5 and S6). This difference was attributed to the atactic structure of the second polymer (*ata*-**PO**),

TABLE 1 Results of polymerization reactions

Entry	**MO** (mmol)	Cat.[a]	Cat. (μmol)	**MO** /Cat.	Temp. (°C)	Yield (%)	$M_n \times 10^{-3}$ [b]	PDI	DP [c]
1	1.7	A	0.5	3400	25	90	12.8	1.54	54
2	1.7	A	0.2	8500	50	88	8.30	1.52	35
3	1.7	A	0.2	8500	25	82	11.2	1.69	47
4	3.4	A	0.2	17000	25	80	16.4	1.55	69
5	5.1	A	0.2	25500	25	45	15.6	1.69	66
6	3.4	B	0.2	17000	25	42	12.7	1.71	54
7	3.4	C	0.2	17000	25	0	–	–	–

[a] A: $Et(Ind)_2ZrCl_2$ B: $(Ind)_2ZrCl_2$ C: $Ph_2C(Cp)(9\text{-fluolenyl})ZrCl_2$. These structures were described in Fig. S1.
[b] Estimated by GPC calibrated on polystyrene standards. [c] Degree of polymerization (based on M_n evaluated by GPC)

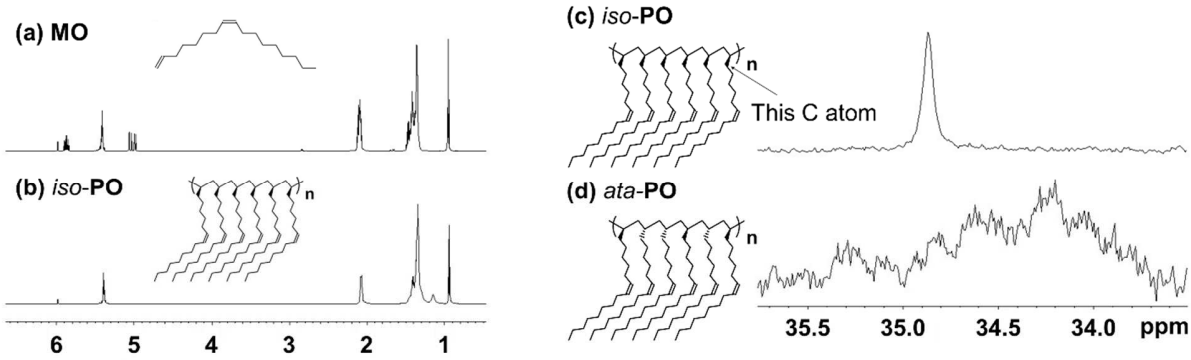


FIGURE 1 ^1H NMR spectra of (a) **MO** and (b) *iso*-**PO** (entry 4) (600 MHz, $C_2D_2Cl_4$, 373 K). $^{13}C\{^1H\}$ NMR spectra of (c) *iso*-**PO** (entry 4) and (d) *ata*-**PO** (entry 6) at the branched carbon atom regions (150 MHz, $C_2D_2Cl_4$, 373 K).

which may arise from the differences in the structures of the catalysts used. In light of previous studies in this field, these results were reasonable.[28] Since signal corresponding to the terminal olefin moiety of the polymer was not observed, β-hydrogen elimination occurred negligibly as a chain transfer reaction due to a transmetalation reaction between the Zr catalyst and MAO. Therefore, site-selective and stereoregular polymerization of **MO** was achieved using Zr metallocene catalysts.

During the curing of unsaturated fatty acids by heat, oxy-radical species form at the internal olefin moieties and attack the neighboring olefin moieties; this is called auto oxidation.[29-30] Since **PO** has a long side chain bearing an internal olefin moiety, its thermal transformation was investigated. While pristine *iso*-**PO** is a viscous liquid at room temperature, it formed a hard and transparent film after thermal treatment on a glass plate at 100 °C for 12 h in air (*iso*-**PO**-**CR**, Supporting Information, Fig. S11). *Iso*-**PO**-**CR** was insoluble in organic solvents, suggesting that thermal cross-linking reaction proceeded at the internal olefin moieties of the side chain of *iso*-**PO**. In contrast to the process in air, no thermal cross-linking was observed when the process was carried out under N_2. Thermogravimetric analysis (TGA) of the thermal transformation of *iso*-**PO** in air (Supporting Information, Fig. S12) showed a weight gain due to oxidation. The FT-IR spectra of pristine *iso*-**PO** and *iso*-**PO**-**CR** in thin-film state (Fig. 2) showed the disappearance of the olefinic C-H stretching peak, and the appearance of carboxy, hydroxy, peroxide, and ether peaks instead. This result indicated the formation of an oxy radical, which underwent subsequent reactions like cross-linking,

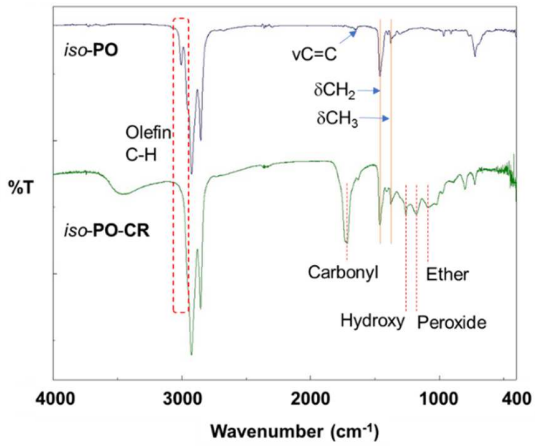


Figure 2 IR spectra of *iso*-**PO** and *iso*-**PO**-**CR**.

carbonylation, and hydroxylation (Supporting Information, Fig. S13).[31] *ata*-**PO** exhibited a thermal transformation similar to that of *iso*-**PO** (Supporting Information, Fig. S14). Considering the durability and transparency (Supporting Information, Fig. S11, S15) of *iso*-**PO**-**CR**, the adhesive performance of thermally cured *iso*-**PO** was examined. Notably, the polymer exhibited adhesion to a glass plate by heating in air. To quantitatively determine the adhesion performance, lap shear tests were conducted on glass and other substrates (Supporting Information, Fig. S16, S17).[32-33] First, the effects of curing temperature and time on the adhesion performance on the glass plate were investigated (Supporting Information, Fig. S16). At a curing temperature of 80 °C, the adhesion was too weak to stand the weight of the glass plate, while higher curing temperature (120 °C) provided better lap shear strength. The lap shear strength of *iso*-**PO**-**CR** on glass increased from 0.026 to 0.16 MPa upon increasing the heating time from 4 to 20 h at 120 °C (Supporting Information, Fig. S16). This indicated that better adhesion performance can be achieved by prolonging the reaction time and increasing the temperature. Moreover, the adhesion performance of *ata*-**PO**-**CR** on the glass substrate (0.080 MPa) was slightly lower than that of *iso*-**PO**-**CR** (Supporting Information, Fig. S16), suggesting that the tacticity of the polymers was associated with their adhesion performance. *iso*-**PO**-**CR** exhibited higher adhesion to aluminum (0.27 MPa) and stainless steel (0.33 MPa), and no adhesion to polyethylene (PE) and polypropylene (PP), due to the interaction of the polar functional groups of **PO**-**CR** with the polar groups on the substrates (Supporting Information, Fig. S17). Therefore, the negligible amount of polar groups on PE and PP would lead to no adhesion.

Herein we demonstrated the facile conversion of oleic acid to a thermally cross-linkable polyolefin based on the unique structure of oleic acid. Pd-catalyzed decarbonylative elimination of oleic acid provided **MO** under mild conditions. Subsequent polymerization of **MO** using the $Et(Ind)_2ZrCl_2$/MAO catalyst proceeded at the terminal olefin moiety in a site-selective and stereoregular manner. The obtained *iso*-**PO** had high isotacticity and long side chain bearing an internal olefin moiety. While pristine *iso*-**PO** was an oily product, its thermal treatment in air led to auto-oxidation and cross-linking at the internal olefin moiety, providing a hard and transparent cross-linked film. Notably, **PO** exhibited adhesion properties to various substrates such as glass, aluminum, and stainless steel. To the best of our knowledge, this is the first report on a method to access reactive functional polyolefins from fatty acids. Therefore, this protocol provides new insights and facilitates the development of biomass-based functional reactive polyolefins. Further investigations on the applicability of this synthetic protocol to other fatty acids, as well as experiments on other chemical transformation of *iso*-**PO**, are currently underway.

EXPERIMENTAL

Synthesis of MO ((8Z)-1,8-heptadecadiene)

A dried 200 mL flask was charged with oleic acid (7.16 g, 25.0 mmol), pivalic anhydride (9.20 g, 50.0 mmol), palladium chloride(II) (133 mg, 0.750 mmol), bis[2-(diphenylphosphino) phenyl] ether (1.21 g, 2.25 mmol), and triethylamine (0.300 mL, 2.30 mmol). *N*,*N*'-dimethylpropyleneurea (50 mL) was added and degassed by 3 times of freeze-pump-thaw cycles. The reaction was

stirred 15 h at 110 °C. After the reaction was complete (monitored by TLC), 200 mL of ethyl acetate was added and the organic layer was washed with 200 mL of saturated ammonium chloride aqueous solution and brine. The product was filtered through an amine functionalized silica gel pad (Φ60 x 50 mm) using hexane as eluent. After concentrating to dryness, crude product was purified by silica column chromatography (Φ50 x 150 mm) using hexane as eluent. After concentrating to dryness, pure product (4.2 g, 71%) was obtained as a transparent oil.
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, δ): 5.84-5.79 (ddt, *J* = 16.8, 10.0, 6.8 Hz, 1H), 5.39-5.33 (m, 2H), 5.02-4.94 (m, 2H), 2.06-2.02 (m, 6H), 1.41-1.27 (m, 18H), 0.89 (t, *J* = 6.9 Hz, 3H) ; ^{13}C{^{1}H} NMR (150 MHz, $C_2D_2Cl_4$, δ):139.1, 130.0, 129.7, 114.2, 33.7, 31.8, 29.7, 29.5, 29.4, 29.2, 28.8, 28.7, 27.1, 27.0, 22.6, 14.1.

Polymerization procedure of isotactic-PO (entry 4 in Table 1)
Et(Ind)$_2$ZrCl$_2$ (5.0 μmol) was dissolved in 2.5 mL toluene. A 20 mL dried greaseless Schlenk tube was charged with dry toluene (2.0 mL), **MO** 803 mg (3.40 mmol), MAO in toluene (0.20 mL, 0.20 mmol-Al), and catalyst solution (0.10 mL, 0.20 μmol). **MO**/MAO/catalyst ratio was 17000:1000:1. The reaction was carried out at 25 °C and was quenched after 24 h by addition of 1 mL methanol and 1 mL of HCl (3.5% in water). The reaction mixture was diluted with 10 mL of $CHCl_3$ and washed two times with 10 mL of distilled water. After drying the organic fraction over Na_2SO_4, the solvent was removed under vacuum. Residual monomer was removed by dissolving the product in $CHCl_3$ followed by precipitation with 300 mL of methanol for 2 days. Subsequently, the product was dried in vacuum. 641 mg of transparent viscous oily product was obtained (yield 80%).
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 373 K, δ): 5.42-5.37 (m, 2H), 2.08-2.06 (br, 4H), 1.51-1.21 (br, 21H), 1.20-1.10 (br, 2H), 0.94 (t, 3H); ^{13}C{^{1}H} NMR (150 MHz, $C_2D_2Cl_4$, 373 K, δ): 129.7, 129.6, 40.4, 34.9, 32.6, 31.6, 29.8, 29.7, 29.6, 29.3, 29.1, 29.0, 27.2, 27.1, 26.4, 22.3, 13.7.

Polymerization procedure of atactic-PO (entry 6 in Table 1)
(Ind)$_2$ZrCl$_2$ was synthesized referring to reported procedure.[27] (Ind)$_2$ZrCl$_2$ (5.0 μmol) was dissolved in 2.5 mL toluene. A 20 mL dried greaseless Schlenk tube was charged with **MO** 803 mg (3.40 mmol), MAO (0.20 mmol), and catalyst solution (0.10 mL, 0.20 μmol). **MO**/MAO/catalyst ratio was 17000:1000:1. Polymerization and purification were conducted with same procedure to above.
^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 373 K, δ): 5.43-5.37 (m, 2H), 2.08-2.06 (br, 4H), 1.58-1.10 (br, 23H), 0.94 (t, 3H); ^{13}C {^{1}H} NMR (150 MHz, $C_2D_2Cl_4$, 373 K, δ): 129.7, 129.6, 41.6-40.5(br), 34.9-33.6(br), 32.9, 31.6, 29.8, 29.7, 29.6, 29.3, 29.1, 29.0, 27.2, 27.1, 26.4-25.8(br), 22.3, 13.7.

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